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Reduction of CFC Usage in U.S. Exempted and Excluded Aerosols

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16. ABSTRACT The paper examines products exempted and excluded from the 1978 U.S. ban on the use of chlorofluorocarbons (CFCs) as aerosol propellants. Consumption of CFCs still utilized for these products in the U.S. amounts to about 25.5 million lb (11.6 million kg) per year. Alternative formulations which may be used to reduce or eliminate the CFC content of these products are discussed. It is technically feasible to replace about 40% of the CFC usage in these products with alternative propellants available today. However, seven categories of products are identified for which immediate replacement of all of the CFC content is not technically feasible. Complete CFC replacement in these products must await the commercialization of newer substitute chemicals currently being developed by industry. Nevertheless, some reformulation is possible in the interim for some of the seven categories, allowing reduced CFC usage.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Chlorohydrocarbons	Stationary Sources	07C
Fluorohydrocarbons	Chlorofluorocarbons	
Substitutes		14G
Aerosols		07D
Propellants		21I

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REDUCTION OF CFC USAGE IN U.S. EXEMPTED AND EXCLUDED AEROSOLS

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INTRODUCTION

In March 1978, nearly 10 years before the "Montreal Protocol on Substances That Deplete the Ozone Layer," (1) the United States Environmental Protection Agency (EPA) together with the Food and Drug Administration (FDA) promulgated a general ban on the use of fully halogenated chlorofluorocarbons (CFCs) used as propellants in aerosol products. On the basis of the amount of CFCs used as aerosol propellants (roughly 50 percent of all U.S. CFC production in 1975) and the potential health effects resulting from CFC-related ozone depletion, it was decided that continued use of CFCs as aerosol propellants represented an unreasonable risk to human health and the environment.

During the time of the 1978 rulemaking activity, the EPA also considered the risks associated with nonpropellant uses of CFCs; for example, use as solvents, foam blowing agents, and refrigerants. However, a decision was made by the Agency to delay action on a finding of unreasonable risk associated with nonpropellant uses of CFCs in order to lessen the immediate overall regulatory burden. Exemption of certain aerosol products was allowed if it could be shown that no alternatives were available, and that the products had "essential" applications. This allowance was also viewed as lessening the overall regulatory impact as was the delaying of the effective date of the ban until 18 months after the original proposal date (May 1977).

While it was noted that depletion of the ozone layer was a global problem and that other countries might not take the same regulatory measures as the U.S., the EPA and FDA felt that the similar actions by other nations would not occur unless the U.S., as the largest aerosol producing and consuming nation, took the initiative.

Consumers were also expressing their concern through the marketplace. A 40 percent decline in CFC sales for aerosols had already occurred in the previous 3 years. This was taken by the agencies as evidence that the public supported the regulatory action, and that acceptable alternatives either as mechanical dispensing devices or other propellants were available in most cases.

Today, as a result of the 1978 CFC propellant ban, approximately 81 percent of U.S. aerosols are pressurized with hydrocarbons (propane, n-butane, iso-butane, or their blends). Another 7 percent use carbon dioxide, and the remaining 12 percent use nitrous oxide, CFCs, dimethyl ether (DME), nitrogen, HFC-152a, and HCFCs (hydrogenated CFCs) in approximately that order. The few CFC aerosols remaining in use in the U.S. are those permitted by special exemption or by exclusion from the regulation. Potential alternatives for these exempted and excluded products will be discussed later in this paper.

By 1981, Norway and Sweden had also banned the use of CFCs in aerosols, and Canada passed regulations eliminating CFC propellants from certain toiletries such as underarm deodorants and hair sprays. The European Economic Community (EEC) asked for a voluntary 30 percent reduction in aerosol CFC uses

based on 1976 levels. Nevertheless, as of 1986 the consumption of CFCs for aerosol products worldwide was approximately 300,000 metric tons (MT). Consumption of this tonnage is broken down by world region as shown in Figure 1. This figure is taken from a June 1989 report to the United Nations Environment Programme submitted in response to the periodic technical assessments required by the Montreal Protocol (2). Since aerosol CFC consumption in some regions such as the Soviet Union and Eastern European countries could only be estimated, there is some uncertainty in these numbers. This uncertainty is reflected in the slice of the pie chart designated as unallocated (12.8 percent).

Due to the preponderance of new information on the loss of ozone in the stratosphere not only over Antarctica but globally, a general consensus is developing that CFC usage should be completely phased out. Consequently, CFC aerosol consumption is being rapidly curtailed in many countries today. For example, in April 1989, the EEC concluded a voluntary agreement with the European aerosol industry to reduce by 90 percent the use of CFCs from the 1976 level by December 1990. Most countries still allow certain exemptions for CFC use in aerosol products where no acceptable substitutes are apparent or where the CFC is deemed "essential" to accomplish the intended purpose of the product.

CURRENT U.S. CFC USAGE IN AEROSOLS

Table I shows by product category the number of units (containers) of aerosol products produced in the U.S. in 1987. These data have been adapted from a 1987 survey of pressurized products conducted by the Chemical Specialties Manufacturers Association (CSMA) (3). The list does not, however, include the 68 million cans of refrigerant CFC-12 for recharging auto air conditioners. Categorized in this way, the table shows that only two categories of products in the U.S. still utilize CFCs either as propellants or solvents, or as the sole active ingredient. Thirty-one percent of the automotive/industrial aerosols are determined to contain CFCs as well as 69 percent of the pharmaceutical/medicinal products. In terms of CFC quantities consumed in U.S. aerosol products in 1987, this amounts to approximately 25 million pounds (11,350 MT). Another 67 million pounds (30,000 MT) would be added if one includes the air-conditioning recharge cans which contain 14-16 ounces (397-454 g) each of 100 percent CFC-12 refrigerant. Roughly 15 percent of the 25 million pounds is utilized by the metered-dose inhalation drug (MDID) products.

The products displayed in Table II, which still utilize CFCs, reflect the various exemptions from the 1978 U.S. ban which have been approved by the EPA and FDA. However, not all of the products listed are still in use today. For example, water-based hydrocarbon formulations have virtually replaced the CFC formulations for flying insect pesticides for commercial food handling areas. (This situation does not pertain for flying insect pesticides for aircraft fumigation due to restrictions imposed by the American Pilots Association.) CFC-115 is no longer utilized for whipped food aerosol products but has been replaced by nitrous oxide in specially designed cans. Likewise, no use of CFCs in diamond grit sprays is evident today.

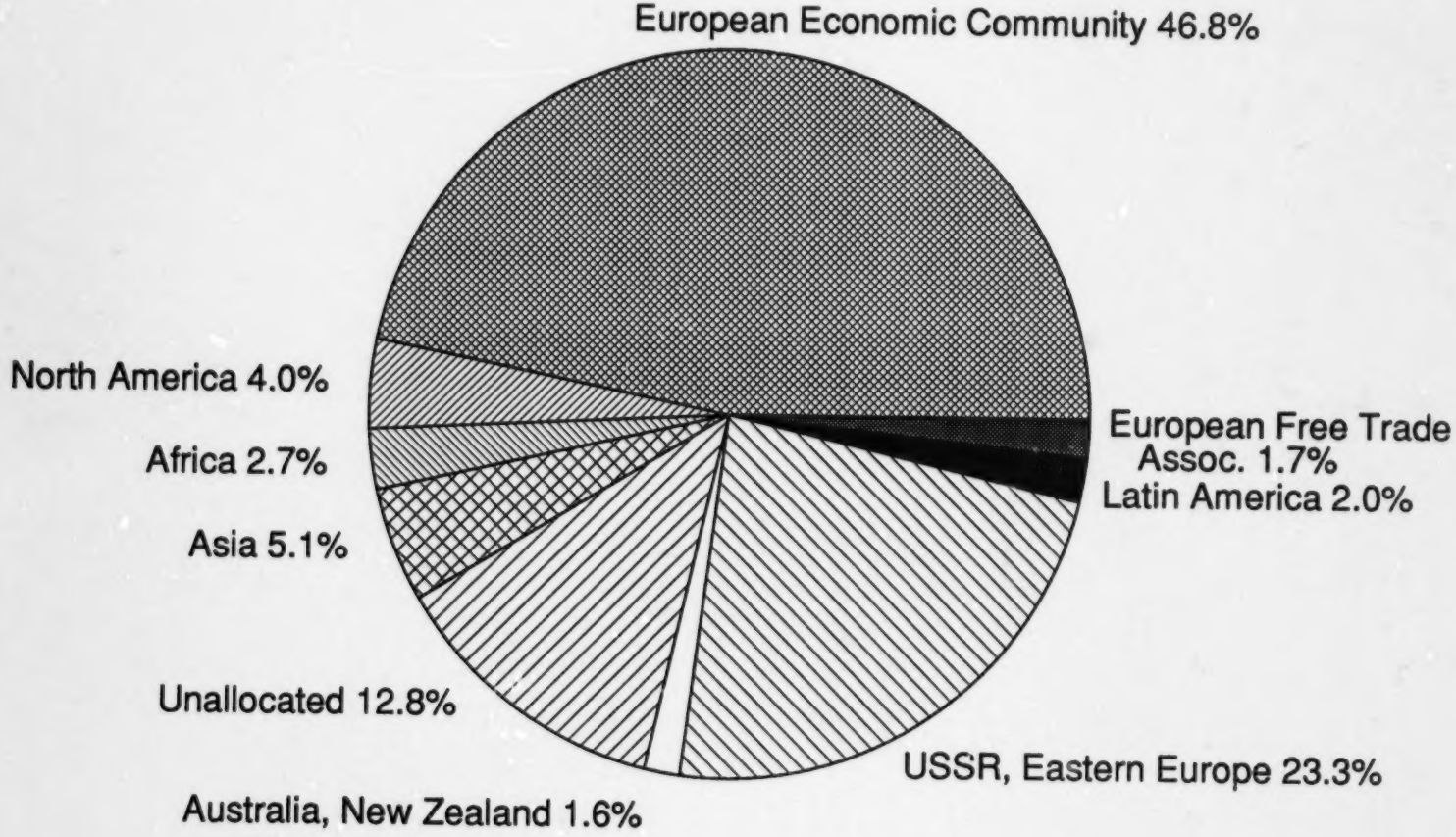

Figure 1. Consumption of CFCs In Aerosols By World Region, 1986
(Total Usage = 300,000 metric tons)

Table I. U.S. Aerosol Production by Product Category, 1987

Sector	Million Units	% of Total	% With CFCs
Personal Products	964	34.7	0
Household Products	640	23.0	0
Automotive/Industrial*	312	11.2	31
Paints/Finishes	307	11.0	0
Insecticides	190	6.8	0
Food Products	140	5.1	0
Pharmaceuticals/Medicinals	126	4.5	69
Animal Products	22	0.8	0
Miscellaneous	80	2.9	0
Total	2,781	100.0	100

*Auto air conditioner recharge units excluded

Table II. U.S. Exempted CFC-Aerosols

1. Mold release agents (e.g., in molds for making plastic medicinal products)
2. Lubricants for pharmaceutical pill press-punches
3. Lubricants, cleaners, dusters, or coatings for electronic/electrical equipment
4. Mercaptan stench warning devices
5. Other warning devices such as intruder alarms, boat horns
6. Flying insect pesticides for commercial food handling areas
7. Flying insect pesticides for commercial aircraft
8. Insect sprays for tobacco barns
9. Metered dose inhalant drugs
10. Contraceptive vaginal foams for human use
11. Aerosols for maintenance and operation of aircraft
12. Aerosols necessary for U.S. military preparedness
13. Diamond grit sprays
14. CFC-115 in puffed/whipped food products

The rationale for exempting these products from the general ban poses an interesting study but is not discussed here. Instead, the interested reader is referred to a recently published EPA report which chronicles these exemptions and suggests alternative formulations to reduce CFC usage (4). However, in general, exemptions have been granted for a number of reasons including:

- Need for a nonflammable product
- Limited production of product and minimal CFC use
- Lifesaving or property-preserving utility of the product
- Solvency and purity requirements

The exemption process still continues today. As late as 1988, the Upjohn Company petitioned the FDA for an exemption for a hair restorer to be marketed as a quick-breaking foam in an aerosol package. The company presented both CFC and hydrocarbon formulation options to the FDA, and the Agency approved only the CFC formulation.

In addition to the products containing CFC propellants which were exempted from the 1978 U.S. ban, a number of aerosols were excluded from the ban by virtue of the CFCs being the sole ingredient or serving some purpose other than as a propellant. In subsequent clarifications of the 1978 regulation, the EPA and FDA held as mutually exclusive the terms "propellant" and "product." This allowed continued or new use of CFCs in aerosol packages wherever the CFC could legitimately be called the product itself or part of the product serving a purpose other than as the expulsion agent. Table III lists the various aerosol products which have assumed this exclusionary privilege since 1978.

Table III. U.S. Excluded CFC-Aerosols

1.	Polyurethane insulation foam products
2.	Tire inflators
3.	Certain specialty foams, whips, and puffs
4.	Medical solvent products (e.g., silicone-based bandage adhesives and removers)
5.	Small refrigeration and air-conditioning recharge units
6.	Drain openers
7.	Microscope slide cleaners
8.	Electronic component cleaners and dusters
9.	Boat horns and other sonic warning devices
10.	Personal (4-15 oz or 113-425 g) halon fire extinguishers
11.	Skin chillers for medical purposes

Again, some of the products listed here are no longer marketed today in part because of customer dissatisfaction with the product (e.g., drain openers). The halon fire extinguishers listed are not true CFC products but can be properly called aerosol products as when marketed as the twin packs of 4-15 ounce canisters in a belt carrier with a common actuator. The halons are also potent ozone depleters.

RESULTS

As CFCs become increasingly scarce and more expensive, marketers of the exempted and excluded aerosols will undoubtedly be searching for alternatives. EPA recently completed an analysis of such alternatives and has published a report (4) which details suggested reformulations to reduce dependence on CFCs for these products. This study revealed that, because of a requirement for extreme compound purity, nonflammability, need to dispense a particular particle size distribution, very low toxicity, compatibility with other materials, or some combination of these, complete substitution of CFCs is not immediately possible for seven product types. For these seven types of products, complete replacement of the CFC content must await commercialization of some of the promising new HFCs or HCFCs now under development such as HCFC-123, HCFC-141b, HFC-134a, and HCFC-124. (In addition to having physical and chemical properties akin to the CFCs, they are designed to replace these newer HFCs, and HCFCs are not regulated as volatile organic compounds (VOCs) by the EPA.) Nevertheless, for several of these seven product types, interim reductions in CFC content (or reductions in the product's ozone depletion potential) are technically feasible.

These seven products are listed in Table IV. Together, these products consumed 15 million pounds (6,800 MT) of CFCs in 1987 in the U.S. (or 60 percent of the total quantity of CFCs employed in aerosols).

Table IV. Products Judged Most Difficult to Eliminate CFCs in the Near Term

1.	Certain mold release products (e.g., for molds used in making plastic medicinal products)
2.	Lubricants for electronic and electrical applications
3.	Lubricants for pharmaceutical pill and tablet presses
4.	Solvent cleaners and dusters for electrical/electronic equipment
5.	Metered dose inhalant drugs
6.	Contraceptive foams for human use
7.	Solvents for medical use

For all other types of products still utilizing CFCs (representing roughly 40 percent of the total CFC quantity used in aerosols in the U.S.), total elimination of the CFC content is technically feasible immediately. Table V lists some of the important factors which must be considered in developing alternative formulations for aerosols. The list is illustrative rather than exhaustive.

Table V. Considerations in the Development of Non-CFC Formulations

1.	Availability of alternative chemical(s)
2.	Control of flammability
3.	Desired particle size distribution
4.	Compatibility with dispenser materials
5.	Organoleptic stability
6.	Pressure limitations
7.	Product utility or efficacy for intended uses
8.	Spray rate and use-up rate
9.	Toxicity
10.	Environmental impact
11.	Cost

Since 1983, a set of four nonhydrocarbon alternatives to CFCs has been commercialized. These currently available alternatives are shown in Table VI along with some of their pertinent properties. Note that all four compounds are gases at room temperature. Boiling points are -10°C or lower; therefore, none can be considered a direct replacement for CFC-11 (B.P. = 23.8°C) or CFC-113 (B.P. = 47.6°C) which are liquids at room temperature.

Table VI. Properties of Currently Available Nonhydrocarbon, Non-CFC Propellant Alternatives

Propellant:	HCFC-22	DME	HFC-152a	HCFC-142b
Formula	$CHClF_2$	$(CH_3)_2O$	CHF_2-CH_3	$CClF_2-CH_3$
Pressure (bar) @21°C	8.3	4.3	4.3	2.0
Pressure (bar) @ 54°C	20.5	12.0	12.2	6.7
B.P. (°C)	-41	-25	-25	-10
LEL-UEL* (%)	non-flammable	3.3-18	4-17	7-15
Solubility in water (%)	3	35	1.7	0.5

* LEL, UEL = Lower and Upper Explosion Limits, respectively, as wt% of compound in air

Whenever hydrocarbons fail to meet the propellant criteria required for a product, these alternatives should be considered. Dimethyl ether (DME) is currently employed in about 2 percent of the total aerosol market in the U.S. and more extensively in Europe and Japan. Its excellent solvent properties are frequently as important as its propellant features in aerosol products. It is quite soluble in water, allowing formulations in which the DME/water mix serves both as solvent and propellant. DME costs about 2 to 3 times as much as hydrocarbon propellants.

HFC-152a has as its main drawbacks its relatively high cost (about 10-13 times more expensive than hydrocarbons), and the fact that it is flammable. Because of this, HFC-152a enjoys only very limited use at present. In fact, the higher cost of the available nonhydrocarbon, non-CFC propellants is often the main deterrent to their increased usage.

The two HCFCs (-22 and -142b) can also be utilized as blends with each other or with hydrocarbons. A 40:60 (weight %) blend of HCFC-22/142b is nonflammable, has a vapor pressure of about 63 psig (4.3 bar) at 21°C (70°F), and therefore compares well with CFC-12 which is nonflammable and has a vapor pressure of 70.69 psig (4.9 bar) at 21°C. An example of how conveniently this blend can replace CFC-12 is illustrated below for a mold release agent where product purity, propellant volatility, and nonflammability are key properties:

Current CFC Formula	HCFC/CFC Formula (Option A)
3 % Concentrate*	3 % Concentrate
57 % CFC-11	54 % CFC-11
40 % CFC-12	28 % HCFC-142b
	15 % HCFC-22

* Concentrate refers to the active ingredient; for example, lecithin. All percentages are weight %.

Additional latitude is allowed formulation chemists to explore other advantages as in the following additional options for the mold release product:

Option B	Option C
3% Concentrate	3% Concentrate
40% CFC-11	60% CFC-11
57% HCFC-142b	21% HCFC-142b
	16% HCFC-22

Option D	Option E	Option F
3% Concentrate	3% Concentrate	3% Concentrate
75% CFC-11	91% CFC-11	88% CFC-11
22% HCFC-22	6% CO_2	9% Propane A-108

Compared with Option A, Option B would have a lower density, reduced CFC-11 content, and be more costly. Option C would have lower cost than Option A but a slightly higher density and a higher CFC-11 content. Options D, E, and F would be increasingly less costly alternatives, but provide less CFC-11 reductions than Options A-C. To replace the CFC-11 in the product, one interim option would involve substituting CFC-113 for CFC-11 as in the formula:

Option G

3% Concentrate
35% CFC-113 (purified)
62% HCFC-142b

The advantage of Option G is that CFC-113, though a controlled compound, has a slightly lower ozone depletion potential than CFC-11. On the negative side, the CFC-113 formula is significantly more costly than the other options. When traces of inhibitors such as nitromethane or 1,4-dioxane are not a problem, an alternative formulation might be:

Option H

3% Concentrate
37% 1,1,1-Trichloroethane* (with inhibitors)
36% HCFC-142b
24% HCFC-22

* 1,1,1-trichloroethane is also known as methyl chloroform.

The inhalant drug aerosols cannot be reformulated in this way due to technical difficulties accompanying the use of HCFC-22 such as:

- Greater solvency. This could cause a greater drug tide to be carried through the prealveolar tubes, leading to possible "toxic shock" effects. Also, the higher solvent power of HCFC-22 could result in dissolution of the microcrystalline drug powder followed by larger crystal growth over time (Ostwald ripening). This in turn could lead to reduced delivery of the drug to the subcilial pulmonary regions of the lungs where it is needed.

- Reduced liquid-phase density. This could cause faster settling of the solid drug in the powder dispersion formulas that make up about 90 percent of the industry sales volume. Also, 10-15 percent (by weight) higher levels of the drug and excipients would be required.

- Higher vapor pressure. This would increase the product pressure above that presently permitted by the Department of Transportation for interstate shipment of aerosols; i.e., 180 psig (12.4 bar) at 40°C (130°F).

Additionally, any new pharmaceutical formulation must go through the FDA Amended New Drug Application approval procedures—a process which may take 3 to 5 years. Accordingly, a coalition of 17 companies involved in the development, production, or sale of MDIDs was formed last year to intensify the search for CFC alternatives for these pharmaceutical products. The coalition recognizes the need to phase out CFCs, but also stresses that the lifesaving features of these products be weighed against the adverse health effects resulting from loss of stratospheric ozone.

CONCLUSIONS

In conclusion, it is technically feasible to reduce CFC consumption in those aerosol products still using CFCs in the U.S. by as much as 40 percent in the near term. The remaining 60 percent of CFCs are consumed by seven types of aerosol products for which the replacement of the CFC content is judged more difficult. However, for many of these latter product types, interim reductions of CFCs are possible. While the cost of the nonhydrocarbon alternatives will continue to be substantially higher than the current cost of CFCs, this cost difference will diminish as the availability of CFCs declines. When the aerosol package and its contents are truly "essential" for a particular end-use, these higher costs can be passed on to the consumer. For products which now rely on the unique features of CFC-113 as a highly pure, noncorrosive, nonflammable liquid of moderate solvent strength, and for the MDIDs, complete replacement of the CFC content will likely depend on the commercialization and successful field testing of the future HCFCs and HFCs being developed by chemical producers. In addition, the MDIDs as well as all pharmaceutical aerosol products (including contraceptive foams and skin chillers) must be subjected to a 3 to 5 year FDA approval process.

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